Giant dielectric nonlinearities at a magnetic Bose–Einstein condensation

K. Yu. Povarov,* A. Reichert, E. Wulf, and A. Zheludev†
Neutron Scattering and Magnetism, Laboratory for Solid State Physics, ETH Zürich, Switzerland‡

(Dated: October 21, 2015)

We experimentally investigate the dielectric response of the low-dimensional gapped quantum magnet $Cu_2Cl_4{\cdot}H_8C_4SO_2$ near a magnetic field-induced quantum critical point, which separates the quantum-disordered and helimagnetic ground states. The observed magnetocapacitive effect originates from an *improper* ferroelectric nature of the transition, which itself is perhaps one of the best known realizations of Bose–Einstein condensation of magnons. Despite that, we find that the magnetocapacitive effect associated with the transition exhibits huge and very unusual anharmonicities.

PACS numbers: 75.10.Kt,75.10.Jm,75.85.+t,77.22.-d

The phenomenon of magnetic Bose–Einstein condensation (BEC) is one of the most fascinating analogies between the properties of quantum magnets and bosonic systems [1, 2]. It corresponds to spontaneous long-range ordering induced in gapped quantum paramagnets by external magnetic fields. Since conventional BEC is a spontaneous breaking of $U(1)$ gauge symmetry, a crucial requirement for the magnetic analog is the presence of isomorphous $SO(2)$ axial spin rotation symmetry in the disordered phase. Unfortunately, symmetry-breaking anisotropic interactions that are always present in real crystalline materials preclude the applicability of the BEC concept close to the quantum critical point. The only exception would be the case of incommensurate helimagnetic order. Here, the required $SO(2)$ symmetry is robust, as it represents a sliding of the magnetic spiral with respect to the crystal lattice, made "frictionless" by its incommensurability. There is, however, a potential complication. Helimagnets are likely to be multiferroic [3]. In a spiral structure, the lack of inversion symmetry between the spins gives rise to electric polarization [4–6]. The intrinsic coupling between magnetic and electric degrees of freedom is a complication that can potentially modify the very nature of the quantum critical point (QCP). A few recent studies looked at rare cases in which multiferroicity occurs at quantum phase transitions (QPTs) [7–9], but not much work was done to study the criticality of such transitions. Moreover, the very important case of QCPs connecting magnetically ordered and quantum-disordered phases remains largely unexplored in the context of multiferroic physics. The two questions to be addressed are as follows: (i) Can this type of transition be described as BEC and (ii) how do the dielectric properties behave at and beyond the QCP?

On the experimental side, some progress has occurred very recently with the discovery of the $S = 1/2$ quasi-one-dimensional quantum antiferromagnet $Cu_2Cl_4{\cdot}H_8C_4SO_2$ (also known as Sul-Cu_2Cl_4) [10–13]. This material features a magnetic-field-induced QPT from a quantum-disordered to a helimagnetic state. However, previous studies have portrayed this transition as being more complex than a simple magnetic BEC. Dielectric spectroscopy experiments [14] pointed to the possibility of a dielectric susceptibility divergence at $T = 0$. At the same time, the shape of the phase boundary and the order parameter exponent were found to be inconsistent with the BEC paradigm [10, 12]. This indicated the possibility of an unconventional order parameter involving both spin and charge degrees of freedom. In the present Rapid Communication, we show that this is *not* the case, and that electric polarization in Sul-Cu_2Cl_4 is *not* a true order parameter of the transition. We show that the QCP is a "protected" BEC of magnons, and is arguably the only clean realization of such among all known materials. While electric polarization plays a dependent role, its behavior is far from trivial. Near the magnetic QCP in Sul-Cu_2Cl_4, we find spectacular anomalies in the *nonlinear* dielectric response.

Sul-Cu_2Cl_4 belongs to a family of insulating metaloorganic Heisenberg spin systems. Its magnetic properties are due to $S = 1/2$ Cu^{2+} ions. The spins are antiferromagnetically coupled into one-dimensional structures, which can be described as highly frustrated four-leg spin tubes, running along the c axis of the triclinic structure (see Refs. [11, 12] for more details). This layout, with an even number of "legs", is responsible for the nonmagnetic quantum-disordered ground state, and a gap $\Delta \simeq 0.52$ meV in the spin excitation spectrum. Due to a geometric frustration of the exchange interactions, the dispersion minimum for the triplet of lowest-energy $S = 1$ excitations occurs at an incommensurate wave vector. As a result, in an external magnetic field $H_c = \Delta/g\mu_B \sim 3.7$ T for $\mathbf{H}||\mathbf{b}$, Sul-Cu_2Cl_4 undergoes a soft-mode ordering transition with a propagation vector $\mathbf{Q} = (-0.22, 0, 0.48)$ [12, 13]. The structure of the ordered high-field phase has been resolved by neutron diffraction [12]. The spin components transverse to $\mathbf{H}$ form a spiral such that $\langle \mathbf{S}_\perp(\mathbf{r})\rangle = \mathbf{S}_1 \cos(\mathbf{Qr})+\mathbf{S}_2 \sin(\mathbf{Qr})$ with $\mathbf{S}_1 \perp \mathbf{S}_2$. This spiral arrangement lacks an inversion symmetry and hence induces an electric polarization $\mathbf{P} \propto [[\mathbf{S}_1 \times \mathbf{S}_2] \times \mathbf{Q}]$ [4, 5]. To date, this polarization has not been directly measured, and is likely to be extremely small. Instead, previous studies of Schrettle *et al.* [14] probed the corresponding dielectric permittivity ε. The apparent divergence of this quantity at the phase transition was taken as a sign of the critical fluctuations of P, which would imply that the transition is different from simple ordering of localized spins.

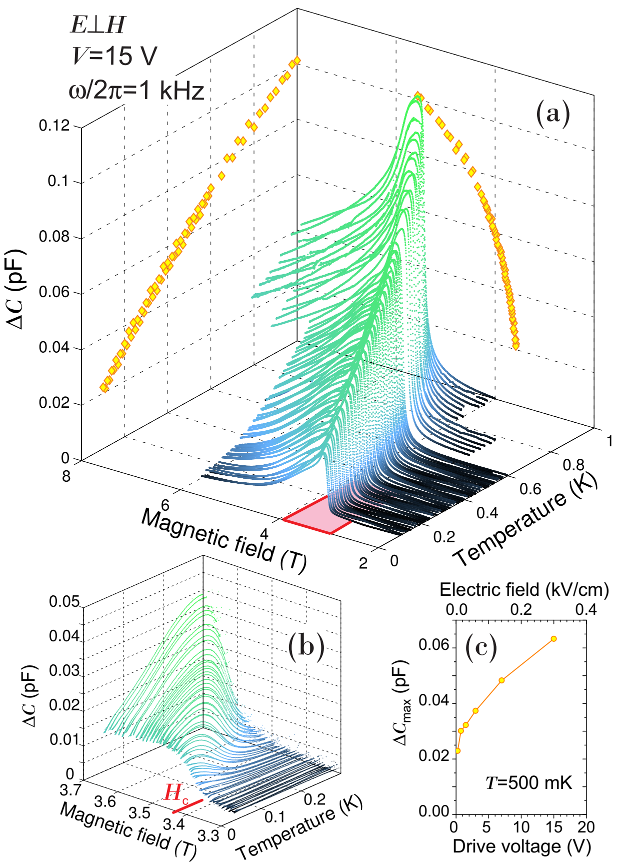

FIG. 1. (Color online) Magnetocapacitive effect in Sul-Cu_2Cl_4. The anomalous contribution to the sample capacitance ΔC is shown as a function of temperature and magnetic field. (a) Field scans at constant temperature. The peak positions and amplitudes are projected onto the $\Delta C-H$ and $\Delta C-T$ planes (yellow diamonds). The highlighted $H-T$ region in close vicinity to the QCP is the domain of temperature scans. (b) Temperature scans. The step in field is 0.002 T. The extrapolated value of the zero-temperature critical field is marked. (c) Measured dependence of the amplitude of the dielectric anomaly on the probing voltage at $T = 500$ mK.

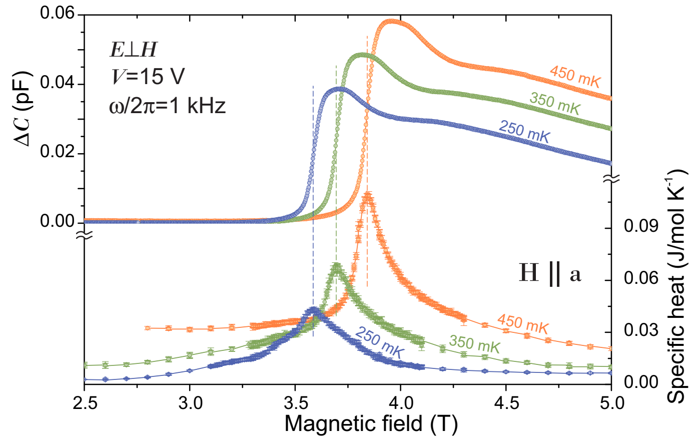

FIG. 2. (Color online) A few representative field scans of a sample capacitance (top), compared to the specific heat data (bottom). For both measurements, $\mathbf{H} \parallel \mathbf{a}$.

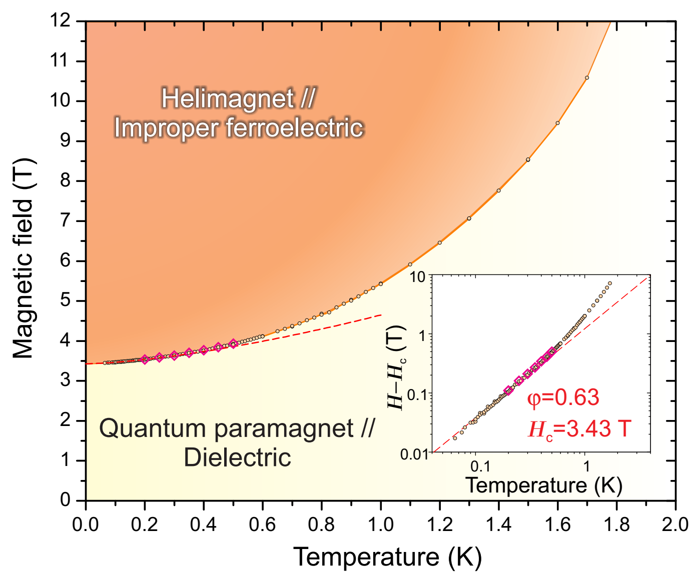

FIG. 3. (Color online) Phase diagram of Sul-Cu_2Cl_4 for $\mathbf{H} \parallel \mathbf{a}$. Small circles are the transition points determined from the magnetocapacitive effect and diamonds are the transition points found from the specific heat λ-anomaly. The solid line is a guide for the eye. The dashed line is a fit to Eq. (1) in the range $T < 300$ mK. The inset shows a logarithmic plot of the measured phase boundary.

The main limitation of that study was in that it only probed temperatures above 1 K, never closely approaching the QCP at $T = 0$. In the present work we have overcome this technical difficulty by combining a capacitance bridge setup similar to that used in Ref. [14] with a ^{3}He-^{4}He dilution refrigerator [15]. What is in fact measured in our experiments is the capacitance of a plate capacitor with a Sul-Cu_2Cl_4 sample in between the plates. At low temperatures in the absence of magnetic field it is dominated by a constant background $C_0 \simeq 3.5$ pF due to the "normal" dielectric permittivity of Sul-Cu_2Cl_4, $\varepsilon \simeq 3$. The quantity of interest is the additional capacitance $\Delta C(H, T)$, which is both temperature and magnetic field dependent near the QCP. It is plotted in Figs. 1(a) and 1(b) and represents the observed magnetocapacitive effect, with a maximal detected $\Delta\varepsilon/\varepsilon \sim 3\%$.

The prominent capacitance peak seen at *high* temperatures is what Ref. [14] must have taken for a divergent ε. In fact, at low temperatures, as the QCP is approached, the anomaly weakens, and transforms into a small and rounded step at $T \to 0$. The peak amplitude of ΔC decreases with the temperature almost linearly, rather than diverging at the QCP. A comparison between the capacitance peaks and λ-anomalies in specific heat for $\mathbf{H} \parallel \mathbf{a}$ (Fig. 2) shows that the transition point corresponds to the inflection point of the $\Delta C(H)$ steep slope. Note that critical fluctuations are prominent in specific heat well below the transition field, while the dielectric

contribution immediately disappears in the disordered phase. Moreover, as shown in Fig. 1(b), there is no detectable change in the dielectric permittivity outside of the ordered phase *even along the critical trajectory* $H = H_c = 3.43 \pm 0.01$ T [15]. We conclude that below H_c there are no critical fluctuations of polarization. The anomalous contribution to dielectric susceptibility is confined to the ordered phase and is triggered by the spontaneous magnetic order. The situation is akin to conventional thermal phase transitions in improper ferroelectrics, where P appears not in a spontaneous way, but as a result of coupling to some other parameter which actually undergoes criticality [16]. Thus, the QCP in Sul-Cu_2Cl_4 is related to the magnetic degrees of freedom alone, while the field-induced phase is an *improper* ferroelectric.

Although ferroelectricity does not drive the QPT in Sul-Cu_2Cl_4, the very precise measurements of ε enable us to extract the critical field with very high accuracy for this compound, and thereby elucidate the nature of the magnetic transition (Fig. 3). The parameter most relevant to the QCP is the so-called crossover exponent φ, which defines the phase boundary at $T \to 0$:

$$H - H_c \propto T^{1/\varphi}. \tag{1}$$

A shrinking fit window analysis [15] of our data reveals that a true power-law behavior extends only up to $T \sim 300$ mK, a range not probed by previous specific heat studies [10, 17]. However, as can be seen from the Fig. 3 inset, our dielectric data are dense and accurate enough to yield a very reliable estimate $\varphi = 0.63 \pm 0.03$ for that fitting range. The anomalous result $\varphi \simeq 0.34$ previously obtained by neutron scattering [12] is likely due to the fact that of the five data points obtained in this study, all except one did lie outside of the true power-law range. Our present result $\varphi \simeq 0.63$ is fully consistent with $\varphi = 2/3$ expected for a magnetic BEC transition [1, 2].

This finding is significant. Indeed, despite numerous claims to the contrary, the field-induced transition in most gapped quantum magnets is, strictly speaking, *not* in the BEC universality class. Instead, due to the magnetic anisotropy which breaks the prerequisite $SO(2)$ symmetry of the Hamiltonian in materials such as $TlCuCl_3$ and IPA-$CuCl_3$, it is actually of the Ising type [18] with an energy gap in the magnetically ordered state [19, 20]. Even in the one known tetragonal compound DTN [21, 22] the transition is likely discontinuous due to magnetoelastic coupling and a spontaneous lattice distortion [18], showing critical exponents inconsistent with BEC [23]. In contrast to all these commensurately ordering materials, the $SO(2) \equiv U(1)$ symmetry in Sul-Cu_2Cl_4 is *protected by its incommensurability*. Indeed, the phase of the incommensurate spiral structure is decoupled from any magnetic anisotropy terms that are commensurate, and the ordered state necessarily has a gapless "sliding mode" [24].

Even though in Sul-Cu_2Cl_4 the charge degrees of freedom do not drive the QCP, the dielectric properties here are quite unusual. A careful examination of the observed magnetocapacitive effect reveals its amazingly nonlinear nature. Just varying the probing voltage leads to a drastic change of the amplitude of the dielectric anomaly, without affecting the onset of the transition or the background C_0. An example of such dependence is shown in Fig. 1(c). The peak magnitude $\Delta C_{\max}$ at a fixed temperature monotonically decreases with a decrease of the voltage. Note that the electrical fields producing this nonlinearity are very modest [upper scale in Fig. 1(c)].

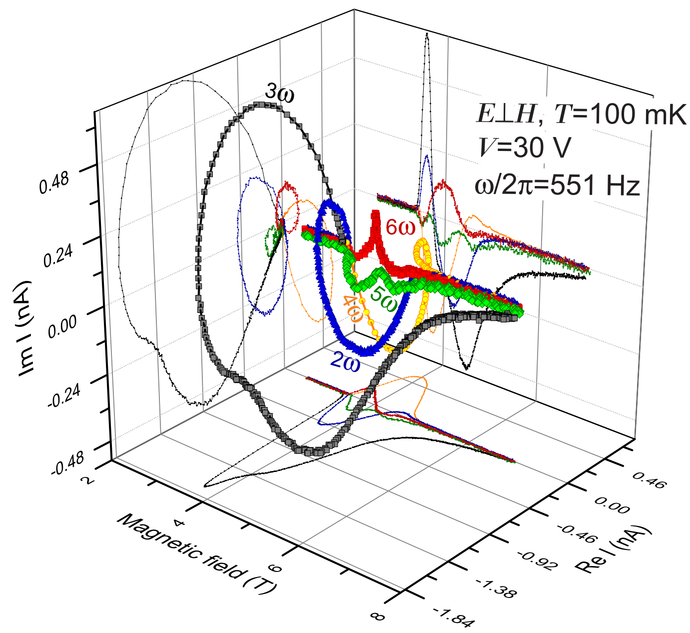

FIG. 4. (Color online) Phase transition in Sul-Cu_2Cl_4 as seen by nonlinear dielectric spectroscopy. Current harmonics $I_n(H)$ (n from 2 to 6) induced by an applied sine voltage are plotted as a functions of magnetic field at $T = 100$ mK. Projections of $I_n(H)$ onto Re-H, Im-H and Re-Im planes are also shown. Drive voltage has amplitude $V = 30$ V and frequency $\omega/2\pi = 551$ Hz.

The best indicators of nonlinear behavior are the higher-order harmonics in ac measurements. In our case of Sul-Cu_2Cl_4, we tracked the complex harmonics of the displacement current, induced by the applied ac voltage [15]. A representative data set (note the low $T = 100$ mK) is shown in Fig. 4. Below the critical field the nonlinear response is zero. However, inside the ordered helimagnetic phase all current harmonics with frequencies up to 6ω show a complicated behavior in the complex plane as a function of applied magnetic field. At still higher fields, they gradually decrease and are eventually suppressed, as is the linear magnetocapacitive effect. Since the displacement charge flow is related to the change of sample polarization $\partial P/\partial t$, the appearance of current harmonics under a periodic voltage $V \sin(\omega t)$ is a direct consequence of the polarization nonlinearity:

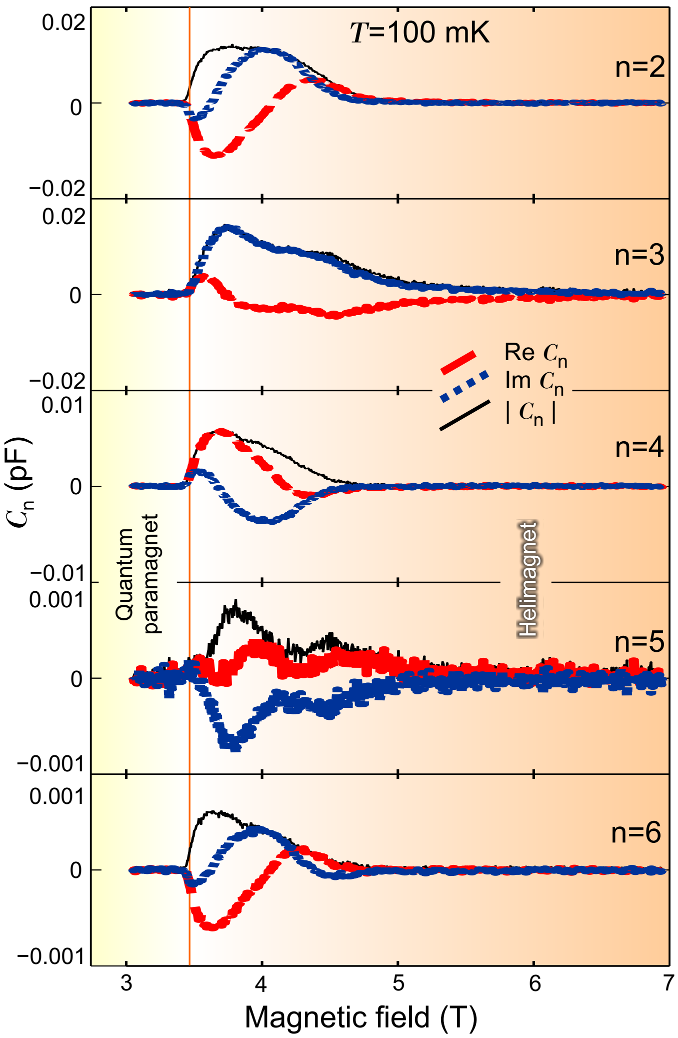

FIG. 5. (Color online) Nonlinear contributions to the magnetocapacitive effect in Sul-Cu_2Cl_4 at $T = 100$ mK C_n (see text) as a functions of magnetic field. Thick dashed red and dotted blue lines are real and imaginary parts of C_n and thin black line is the absolute value. Vertical line marks the phase transition field.

$$P(E) = P_0 + \varepsilon_0 \left(\chi_1 E + \chi_2 E^2 + \chi_3 E^3 + ...\right). \quad (2)$$

In this expansion $\chi_1 = \varepsilon - 1$ is the conventional first-order susceptibility, while $\chi_n = \frac{1}{\varepsilon_0 n!}\frac{\partial^n P}{\partial E^n}$ are the nonlinear hypersusceptibilities. The algebra required to restore the hypersusceptibilities χ_n from current harmonics I_n is summarized in Ref. [25]. To allow a *quantitative* comparison between different hypersusceptibilities (which are of different physical dimensions), we present them in the form of anharmonic capacitance contributions $C_n = \varepsilon_0 \chi_n \frac{S}{d} E^{n-1}$ [15]. The resulting $C_n(H)$ for the representative $T = 100$ mK case are plotted in Fig. 5. By comparing this plot to Fig. 1 one can immediately see that some of the anharmonic contributions have *the same* order of magnitude, as the linear magnetocapacitance term. Already at a very moderate electric field $E \sim 0.3$ kV/cm, the nonlinear response is at least as important as the linear one. Such a giant dielectric nonlinearity at a quantum phase transition of a nonelectric nature is an interesting phenomenon.

A transition-related nonlinear electric response is well documented for proper ferroelectrics and relaxors [26], but not for *improper* ferroelectrics. Previous studies of other Cu^{2+} based $S = 1/2$ improper helimagnetic ferroelectrics, such as $CuCl_2$ [27], $LiCu_2O_2$ [28], and $LiCuVO_4$ [29, 30], have not encountered $P(E)$ nonlinearity at the transition point. A small nonlinearity was typically found deep in the ordered phase as a consequence of a well-developed $P(E)$ hysteresis curve. The direction of P in individual magnetic domains is coupled to the spiral chirality, which can be switched by sufficiently strong E, producing the hysteresis. In Sul-Cu_2Cl_4, a small history dependence of magnetocapacitance above H_c and suppression of the effect by bias field [15] indicate that domains also play an important role. The observed nonlinearity may in principle originate from the extreme sensitivity of the domains to E close to the magnetic order breakdown. Since even tiny amounts of impurities are known to have a huge effect on the phase transition in Sul-Cu_2Cl_4 [17], in the future it will be very interesting to investigate their influence on the dielectric response and domain mobility.

In summary, the field-induced QCP in Sul-Cu_2Cl_4 is a purely magnetic one, and appears to be one of the best realizations of magnetic BEC. The material is thus an "improper quantum field-induced ferroelectric." Its unusual dielectric response is confined to the magnetically ordered phase and is hugely nonlinear, even in very modest drive fields.

We would like to extend our thanks to Prof. B. Batlogg for generously sharing some key equipment for the present experiments, and to Prof. M. Mostovoy for illuminating discussions. Special thanks go out to Dr. S. Gvasaliya for assistance with the instrument development. This work was supported by the Swiss National Science Foundation, Division 2.

SUPPLEMENTAL MATERIAL

I. EXPERIMENTAL DETAILS

The sample for the magnetocapacitive measurements was a co-aligned mosaic of $d \sim 0.5$ mm-thin single crystals of Sul-Cu_2Cl_4 was sandwiched between the copper plates of a capacitor, that were parallel to the crystallographic (ac) plane. This assembly was placed at the sample stage of Quantum Design Physical Properties Measurement System (PPMS) ^{3}He-^{4}He Dilution Refrigerator insert. The magnetic field $\mathbf{H}$ was applied parallel to the $\mathbf{a}$ axis. It defines the spiral plane, the expected polarization being along $\mathbf{b}^* \parallel \mathbf{E}$. Special care was taken to

prevent any exposure of the sample to the atmosphere to avoid deterioration. Measurements were done using an AH2550A capacitance bridge. The capacitor plate area was $A = 8 \times 8$ mm^2. Due to the difficulty of precisely measuring the filling factor of the Sul-Cu_2Cl_4 "effective capacitor", we prefer to report the results as a change in sample capacitance $C = \frac{A}{d}\varepsilon_0\varepsilon$ rather than a change in dielectric permittivity. The values of E and ε mentioned in the text should be considered as estimates.

Nonlinear dielectric spectroscopy was performed on the very same sample assembly during the same experimental run. The source voltage was applied to one of the capacitor plates, and SR7370 lock-in amplifier was used to read the displacement current harmonics. We use the actual value of $V = 30$ V to estimate the hypersusceptibilities χ_n, but smaller voltage $V = 15$ V to present them as nonlinear capacitances C_n for consistent comparison with the bridge data.

Specific heat was measured on $m \simeq 0.1$ mg Sul-Cu_2Cl_4 sample with the help of adiabatic calorimetry option for PPMS ^{3}He-^{4}He Dilution Refrigerator insert. The contribution of Apiezon N grease and silver sample holder was measured in a separate run and subtracted. The measurements extend down to 200 mK; below this temperature the data becomes progressively plagued by huge contributions from nuclear spin specific heat.

II. PHASE DIAGRAM

To investigate the critical properties of the phase boundary, we have performed a windowing analysis, similar to how it has been in Ref. [31]. The dependencies of estimated critical field and crossover exponent φ on the cut-off temperature is shown in Fig. 6. Around $T \sim 300$ mK the dependence of H_c and φ on the threshold temperature vanishes, indicating the true power-law behavior. For extremely narrow fit windows the resulting values are slightly scattered due to the decreasing amount of datapoints. For a wider fitting range $\lesssim 1$ K, we get $\varphi \simeq 0.5$, thus recovering the value previously found by specific heat measurements [10].

The observed critical filed value is different from the one quoted in the introduction, due to the direction of applied field in the present study ($\mathbf{H}||\mathbf{a}$) being different from that in previous neutron [12] and calorimetry [17] experiments ($\mathbf{H}||\mathbf{b}$). Preceding dielectric study [14] also used $\mathbf{H}||\mathbf{a}$ field orientation,and their phase boundary is apparently shifted from the values for $\mathbf{H}||\mathbf{b}$ they quote in Fig. 4.

III. MAGNETOCAPACITIVE EFFECT

A. Symmetry properties

The spiral order in Sul-Cu_2Cl_4 can be parameterized as $\langle \mathbf{S}_\perp(\mathbf{r})\rangle = \mathbf{S}_1\cos(\mathbf{Qr}) + \mathbf{S}_2\sin(\mathbf{Qr})$ with $\mathbf{S}_1 \perp \mathbf{S}_2$. This spiral arrangement, as it has been shown by Mostovoy [5] and Katsura, Nagaosa and Balatsky [4] induces an electric polarization $\mathbf{P} \propto [[\mathbf{S}_1 \times \mathbf{S}_2] \times \mathbf{Q}]$ due to lack of inversion symmetry between the spins and nonzero spin-orbit coupling. This effect is often called "inverse Dzyaloshinskii–Moriya" mechanism, due to analogy with the Dzyaloshinskii–Moriya antisymmetric coupling [32, 33]. In the latter case the asymmetry of the charge distribution between the magnetic ions allows for a coupling term proportional to $[\mathbf{S}_1 \times \mathbf{S}_2]$, which may stabilize a spiral phase. In the former case it is inverse: spiral arrangement of spins enforces spatial asymmetry in charge distribution.

The distinctive feature of this mechanism is the direction of polarization, lying in the spiral plane and perpendicular to the propagation vector $\mathbf{Q}$. Crystals of Sul-Cu_2Cl_4 possess a natural cleavage plane, which is almost parallel to $\mathbf{Q}$, and the spiral plane is fixed by the external magnetic field, as $[\mathbf{S}_1 \times \mathbf{S}_2] \parallel \mathbf{H}$. Hence, such a plane is ideally suited for the observation of magnetocapacitive effect when $\mathbf{H} \perp \mathbf{Q}$ and $\mathbf{E} \perp \mathbf{Q}, \mathbf{H}$ (i. e. $\mathbf{E}$ perpendicular to the "good plane" and magnetic field also lies in the "good plane"). The bulk of the measurements was performed in this crossed fields configuration. However, we also adopted an alternative experimental setup: the same sample assembly was mounted in parallel fields configuration, with $\mathbf{H} \parallel \mathbf{E}$. This means, that the dielectric response is probed perpendicular to the spiral plane. In such configuration the magnetocapacitive effect is drastically suppressed (see Fig. 7): while at $T = 500$ mK a prominent peak is seen in crossed fields configuration, only a tiny remnant peak can be observed in the parallel fields configuration. This indicates that the non-trivial dielectric response is restricted to the spiral plane — exactly what should be expected for the "inverse Dzyaloshinskii–Moriya" mechanism.

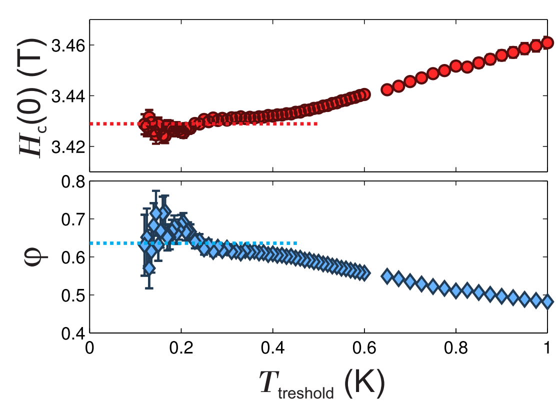

FIG. 6. Windowing analysis of Sul-Cu_2Cl_4 phase boundary obtained from dielectric measurements.

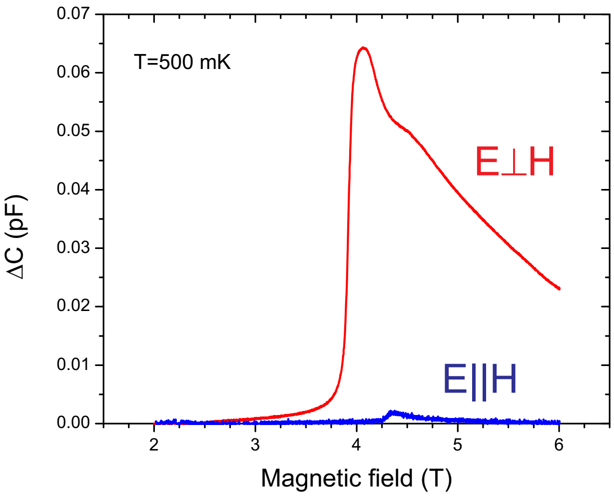

FIG. 7. Magnetocapacitive effect in the same sample of Sul-Cu_2Cl_4, measured along ($\mathbf{E} \perp \mathbf{H}$) and perpendicular ($\mathbf{E} \parallel \mathbf{H}$) to the spiral plane.

B. Domain-related effects

The magnetocapacitive effect, observed in Sul-Cu_2Cl_4, demonstrates a history dependence in the magnetically ordered phase. The example can be found in Fig. 8, where the field is swept from 3 to 6 T and then back at rate of 10^{-3} T/sec. The hysteresis onset is located above the inflection point of the steep slope of $\Delta C(H)$. Going below the critical field "resets" the history, making the curves shown in Fig. 8 fully reproducible over multiple runs. Also, note the suppression of the magnetocapacitive anomaly by a constant (bias) electric field applied to the sample. All together this is a strong indication of domain formation above H_c. In zero electric field one may expect equal population of clockwise and counterclockwise spiral domains, having the opposite direction of electric polarization vector. Note that the spiral plane is fixed by external magnetic field, and hence the polarization of the domains must behave in Ising-like way. Having such domains can be a natural cause for the memory effect in the ordered phase. Also, it explains the suppression of the effect by bias electric field. Such field would decrease the response of P to the AC probing field, as it would fix the preferred direction of domain polarization.

* povarovk@phys.ethz.ch
† zhelud@ethz.ch
‡ http://www.neutron.ethz.ch/

1 T. Giamarchi, C. Rüegg, and O. Tchernyshyov, "Bose-Einstein condensation in magnetic insulators," Nat. Physics **4**, 198 (2008).
2 V. Zapf, M. Jaime, and C. D. Batista, "Bose-Einstein condensation in quantum magnets," Rev. Mod. Phys. **86**, 563 (2014).
3 S.-W. Cheong and M. Mostovoy, "Multiferroics: a magnetic twist for ferroelectricity," Nat. Mater. **6**, 13 (2007).
4 H. Katsura, N. Nagaosa, and A. V. Balatsky, "Spin current and magnetoelectric effect in noncollinear magnets," Phys. Rev. Lett. **95**, 057205 (2005).
5 M. Mostovoy, "Ferroelectricity in spiral magnets," Phys. Rev. Lett. **96**, 067601 (2006).
6 S. Picozzi, K. Yamauchi, B. Sanyal, I. A. Sergienko, and E. Dagotto, "Dual nature of improper ferroelectricity in a magnetoelectric multiferroic," Phys. Rev. Lett. **99**, 227201 (2007).
7 M. Kenzelmann, G. Lawes, A. B. Harris, G. Gasparovic, C. Broholm, A. P. Ramirez, G. A. Jorge, M. Jaime, S. Park, Q. Huang, A. Ya. Shapiro, and L. A. Demianets, "Direct transition from a disordered to a multiferroic phase on a triangular lattice," Phys. Rev. Lett. **98**, 267205 (2007).
8 N. Abe, K. Taniguchi, S. Ohtani, H. Umetsu, and T. Arima, "Control of the polarization flop direction by a tilted magnetic field in multiferroic $TbMnO_3$," Phys. Rev. B **80**, 020402 (2009).
9 J. W. Kim, S. Khim, S. H. Chun, Y. Jo, L. Balicas, H. T. Yi, S.-W. Cheong, N. Harrison, C. D. Batista, J. H. Han, and K. H. Kim, "Manifestation of magnetic quantum fluctuations in the dielectric properties of a multiferroic," Nat. Commun. **5**, 4419 (2014).
10 M. Fujisawa, H. Tanaka, and T. Sakakibara, "Magnetic field-induced phase transition in quantum spin system $Cu_2Cl_4{\cdot}H_8C_4SO_2$," Prog. Theor. Phys. Supp. **159**, 212

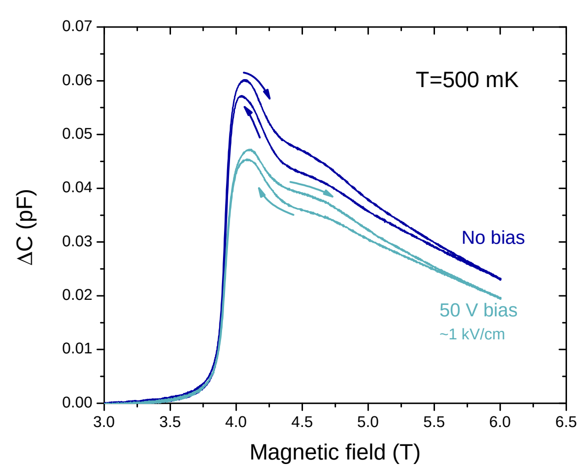

FIG. 8. Examples of hysteretic behavior of magnetocapacitive effect in Sul-Cu_2Cl_4. Also note the suppression of the effect by bias field.

(2005).
[11] V. O. Garlea, A. Zheludev, L.-P. Regnault, J.-H. Chung, Y. Qiu, M. Boehm, K. Habicht, and M. Meissner, "Excitations in a Four-Leg Antiferromagnetic Heisenberg Spin Tube," Phys. Rev. Lett. **100**, 037206 (2008).
[12] V. O. Garlea, A. Zheludev, K. Habicht, M. Meissner, B. Grenier, L.-P. Regnault, and E. Ressouche, "Dimensional crossover in a spin-liquid-to-helimagnet quantum phase transition," Phys. Rev. B **79**, 060404 (2009).
[13] A. Zheludev, V. O. Garlea, A. Tsvelik, L.-P. Regnault, K. Habicht, K. Kiefer, and B. Roessli, "Excitations from a chiral magnetized state of a frustrated quantum spin liquid," Phys. Rev. B **80**, 214413 (2009).
[14] F. Schrettle, S. Krohns, P. Lunkenheimer, A. Loidl, E. Wulf, T. Yankova, and A. Zheludev, "Magnetic-field induced multiferroicity in a quantum critical frustrated spin liquid," Phys. Rev. B **87**, 121105 (2013).
[15] See Supplemental Material for more details.
[16] V. Dvořák, "Improper ferroelectrics," Ferroelectrics **7**, 1 (1974).
[17] E. Wulf, S. Mühlbauer, T. Yankova, and A. Zheludev, "Disorder instability of the magnon condensate in a frustrated spin ladder," Phys. Rev. B **84**, 174414 (2011).
[18] R. Dell'Amore, A. Schilling, and K. Krämer, "$U(1)$ symmetry breaking and violated axial symmetry in $TlCuCl_3$ and other insulating spin systems," Phys. Rev. B **79**, 014438 (2009).
[19] V. N. Glazkov, A. I. Smirnov, H. Tanaka, and A. Oosawa, "Spin-resonance modes of the spin-gap magnet $TlCuCl_3$," Phys. Rev. B **69**, 184410 (2004).
[20] J. Sirker, A. Weiße, and O. P. Sushkov, "Consequences of spin-orbit coupling for the Bose-Einstein condensation of magnons," Europhys. Lett. **68**, 275 (2004).
[21] V. S. Zapf, D. Zocco, B. R. Hansen, M. Jaime, N. Harrison, C. D. Batista, M. Kenzelmann, C. Niedermayer, A. Lacerda, and A. Paduan-Filho, "Bose-Einstein Condensation of $S = 1$ Nickel Spin Degrees of Freedom in $NiCl_2$-$4SC(NH_2)_2$," Phys. Rev. Lett. **96**, 077204 (2006).
[22] L. Yin, J. S. Xia, V. S. Zapf, N. S. Sullivan, and A. Paduan-Filho, "Direct Measurement of the Bose-Einstein Condensation Universality Class in $NiCl_2$-$4SC(NH_2)_2$ at Ultralow Temperatures," Phys. Rev. Lett. **101**, 187205 (2008).
[23] E. Wulf, D. Hüvonen, R. Schönemann, H. Kühne, T. Herrmannsdörfer, I. Glavatskyy, S. Gerischer, K. Kiefer, S. Gvasaliya, and A. Zheludev, "Critical exponents and intrinsic broadening of the field-induced transition in $NiCl_2$-$4SC(NH_2)_2$," Phys. Rev. B **91**, 014406 (2015).
[24] A. D. Bruce and R. A. Cowley, "The theory of structurally incommensurate systems. III. The fluctuation spectrum of incommensurate phases," J. Phys. C: Solid State Phys. **11**, 3609 (1978).
[25] S. Miga, J. Dec, and W. Kleemann, "Computer-controlled susceptometer for investigating the linear and nonlinear dielectric response," Rev. Sci. Inst. **78**, 033902 (2007).
[26] J. Dec, S. Miga, and W. Kleemann, "Ferroelectric phase transitions viewed via nonlinear dielectric response," Ferroelectrics **417**, 82 (2011).
[27] S. Seki, T. Kurumaji, S. Ishiwata, H. Matsui, H. Murakawa, Y. Tokunaga, Y. Kaneko, T. Hasegawa, and Y. Tokura, "Cupric chloride $CuCl_2$ as an $S = \frac{1}{2}$ chain multiferroic," Phys. Rev. B **82**, 064424 (2010).
[28] S. Park, Y. J. Choi, C. L. Zhang, and S-W. Cheong, "Ferroelectricity in an $s = 1/2$ chain cuprate," Phys. Rev. Lett. **98**, 057601 (2007).
[29] M. Mourigal, M. Enderle, R. K. Kremer, J. M. Law, and B. Fåk, "Ferroelectricity from spin supercurrents in $LiCuVO_4$," Phys. Rev. B **83**, 100409 (2011).
[30] A. Ruff, S. Krohns, P. Lunkenheimer, A. Prokofiev, and A. Loidl, "Dielectric properties and electrical switching behaviour of the spin-driven multiferroic $LiCuVO_4$," J. Phys.: Condens. Matter **26**, 485901 (2014).
[31] D. Hüvonen, G. Ballon, and A. Zheludev, "Field-concentration phase diagram of a quantum spin liquid with bond defects," Phys. Rev. B **88**, 094402 (2013).
[32] I. Dzyaloshinsky, "A thermodynamic theory of 'weak' ferromagnetism of antiferromagnetics," J. Phys. Chem. Solids **4**, 241 (1958).
[33] T. Moriya, "Anisotropic Superexchange Interaction and Weak Ferromagnetism," Phys. Rev. **120**, 91 (1960).